The invention relates to the use of polyethylene glycol esters of fatty acids corresponding to the following formula:

\[ R^1 \text{CO} \text{O} \text{(CH}_2\text{CH}_2\text{O})_n \text{OC} \text{R}^2 \]  

where \( R^1 \) and \( R^2 \) independently of one another represent alkyl groups containing 7 to 23 carbon atoms, which may be saturated or unsaturated, linear or branched, and \( n \) is a number of 2 to 50, as lubricants in the processing of thermoplastics.
USE OF POLYETHYLENE GLYCOL ESTERS OF FATTY ACIDS AS LUBRICANTS FOR PLASTICS

RELATED APPLICATIONS

[0001] This application claims priority from EP 06015123.0 filed Jul. 20, 2006, the entire contents of which have been incorporated herein by reference.

FIELD OF THE INVENTION

[0002] This invention relates to the use of polyethylene glycol esters of fatty acids as lubricants for plastics.

BACKGROUND OF THE INVENTION

[0003] In the processing of thermoplastics, lubricants are added as processing aids. On the one hand, the lubricants are capable of reducing the internal friction between plastic particles which makes the plastics easier to melt and promotes the formation of a homogeneous, flowable melt. Lubricants acting in this way are also commonly referred to as internal lubricants. On the other hand, lubricants used in the processing of plastics are capable of reducing the adhesion of the plastic melt to hot surfaces of machine parts or to the walls of the molds. It is assumed that the lubricants, which, after their incorporation in the plastic, migrate from the plastic to the surface on account of their limited compatibility, reduce adhesion. Lubricants acting in this way are also known as external lubricants or as “mold release agents”.

[0004] In principle, the use of the lubricants also has a considerable bearing on the morphology, homogeneity and surface qualities of the plastic products.

[0005] Whether an additive acts as internal or external lubricant depends on many factors, more particularly on its structure and on the nature of the plastic. In many cases, internal and external lubricating effects may even be developed alongside another. Initial observations on lubricants in PVC and their effect as internal and external lubricants can be found in the overview in Gächter/Müller, Kunststoffadditive (2nd Edition, pp. 320-327).

[0006] Known lubricants for plastics include, for example, fatty acids, fatty alcohols, fatty acid esters, fatty acid complex esters, wax esters, dicarboxylic acid esters, amide waxes, metal soaps, montan waxes, hydrocarbon waxes or oxidized hydrocarbons.

[0007] Polyethylene glycol monoesters are used as anti-static and anti-fogging agents in thermoplastics (cf. Antistatic PVC Materials, Shevdyavaev, O.N. USSR, Plasticheskoe Massy (1985), (4), 21-2; ISSN: 0554-2901; in Russian; reported in CAPLUS: 1985:423262).

BRIEF DESCRIPTION OF THE INVENTION

[0008] The problem addressed by the present invention was to provide lubricants, more especially internal lubricants, which could be used in the processing of thermoplastics.

[0009] It has surprisingly been found that polyethylene glycol esters of fatty acids can be used in excellent fashion as lubricants and preferably as internal lubricants in the processing of thermoplastics. The compounds are highly compatible with the polymers and lend during processing to an improvement in the plasticization of the polymer. Another advantage lies in the low inherent volatility of the polyethylene glycol esters of fatty acids.

[0010] The lubricants to be used in accordance with the invention are characterized by the following formula:

\[ R^1-\text{CO-CH}_{2}\text{-CH}_{2}\text{-}OC\text{-R}^2 \]  

in which \( R^1 \) and \( R^2 \) independently of one another represent alkyl groups containing 7 to 23 carbon atoms, which may be saturated or unsaturated, linear or branched, and \( n \) is a number of 2 to 50.

[0011] Accordingly, the present invention relates to the use of polyethylene glycol esters of fatty acids corresponding to the following formula:

\[ R^1-\text{CO-CH}_{2}\text{-CH}_{2}\text{-}OC\text{-R}^2 \]  

in which \( R^1 \) and \( R^2 \) independently of one another represent alkyl groups containing 7 to 23 carbon atoms, which may be saturated or unsaturated, linear or branched, and \( n \) is a number of 2 to 50, as lubricants in the processing of thermoplastics. In a preferred embodiment, \( n \) has a value of 2 to 4.

DETAILED DESCRIPTION OF THE INVENTION

[0012] The term “lubricant” in the context of the present invention denotes lubricants in the broader sense, i.e. external and/or internal lubricants. If a narrower meaning is intended, it is explicitly indicated (i.e. the expression “internal lubricant” is expressly used).

[0013] The compounds (I) to be used in accordance with the invention are preferably used in quantities of 0.05 to 5.0 parts by weight, based on 100 parts by weight of the thermoplastic. The range from 0.1 to 2.0 parts by weight is particularly preferred.

[0014] Suitable \( C_5 \) to \( C_{24} \) fatty acids are both native and synthetic or branched and saturated or unsaturated compounds. The fatty acids may be used in the form of mixtures. Examples of suitable fatty acids are lauric acid, isodecanoic acid, myristic acid, palmitic acid, palmitoleic acid, stearic acid, isostearic acid, oleic acid, elaidic acid, petroselic acid, linoleic acid, linolenic acid, elaeostearic acid, arachic acid, gadoleic acid, behenic acid and erucic acid. Fatty acids containing hydroxyl or keto groups, such as 12-hydroxy stearic acid, are also suitable.

[0015] Fatty acids such as these can be obtained from naturally occurring fats and oils, for example by lipolysis at elevated temperature and pressure and subsequent separation of the fatty acid mixtures obtained, optionally followed by hydrogenation of the double bonds present. Technical fatty acids are preferably used. Technical fatty acids are generally mixtures of different fatty acids of a certain chain length range with one fatty acid as the main constituent, \( C_{12-18} \) fatty acids individually or in admixture are preferably used.

[0016] Basically, there are no restrictions with regard to the thermoplastics. Thermoplastics selected from the group consisting of polycarbonates, polyamides, polysteres, polystyrenes and polyvinyl chloride and copolymers thereof are preferred. These thermoplastics may be stabilized, pigmented, filled with fillers or modified.
In a preferred embodiment, the compounds (I) are used as internal lubricants. All that has been said in the foregoing in regard to the use of the compounds (I) as lubricants also applies to their use as internal lubricants.

Other typical lubricants are C₁₂₋₂₄ fatty acids, C₁₂₋₂₄ fatty alcohols, esters of C₁₂₋₂₄ fatty acids and C₁₂₋₂₄ fatty alcohols (so-called wax esters), esters of C₁₂₋₂₄ fatty acids and polyhydric alcohols containing 4 to 6 hydroxyl groups (so-called polyol esters), dicarboxylic acid esters of dicarboxylic acids and C₁₂₋₂₄ fatty alcohols and complex esters of dicarboxylic acids, polyols and monocarboxylic acids. The standard lubricants mentioned may be used both individually and in admixture with one another.

The following observations apply to the optional other lubricants different from the compounds of formula (I).

Suitable C₁₂₋₂₄ fatty acids are both native and synthetic, linear saturated compounds. If fatty acid mixtures are used, they may contain unsaturated fatty acids. Examples of suitable fatty acids are lauric, tridecanoic, myristic, pentadecanoic, palmitic, margaric, stearic, behenic and lignoceric acid. Fatty acids containing hydroxy groups, such as 12-hydroxystearic acid, are also suitable. Fatty acids such as these can be obtained from naturally occurring fats and oils, for example through lipolysis at elevated temperature and pressure and subsequent separation of the fatty acid mixtures obtained, optionally followed by hydrogenation of the double bonds present. Technical fatty acids are preferably used here. They are generally mixtures of different fatty acids of a certain chain length range with one fatty acid as the main constituent. C₁₂₋₁₈ fatty acids individually or in admixture are preferably used.

The C₁₂₋₂₄ fatty alcohols are mostly linear saturated representatives which may be obtained inter alia from naturally occurring fats and oils by transesterification with methanol, subsequent catalytic hydrogenation of the methyl esters obtained and fractional distillation. Examples of such fatty alcohols are lauryl, myristyl, cetyl, stearyl and behenyl alcohol. These compounds may be used individually and in admixture with one another. Technical fatty alcohols are preferably used. They are normally mixtures of different fatty alcohols of a limited chain length range in which one particular fatty alcohol is present as the main constituent. Technical C₁₂₋₁₈ fatty alcohol mixtures are preferred.

Other suitable additional lubricants are wax esters, i.e. esters of C₁₂₋₂₄ fatty acids and C₁₂₋₂₄ fatty alcohols which preferably correspond to formula (II):

\[
R^1\text{CO-OR}^2
\]

in which \( R^1 \text{CO} \) is a saturated and/or unsaturated acyl group containing 12 to 24 and preferably 12 to 18 carbon atoms and \( R^2 \) is an alkyl and/or alkenyl group containing 12 to 24 and preferably 12 to 18 carbon atoms. Typical examples are esters of lauric acid, isotridecanoic acid, myristic acid, palmitic acid, palmitoleic acid, stearic acid, isostearic acid, oleic acid, elaidic acid, petrosellic acid, linoleic acid, linolenic acid, elaeostearic acid, arachidic acid, gadoleic acid, behenic acid and erucic acid and technical mixtures thereof with lauryl alcohol, isotridecyl alcohol, myristyl alcohol, cetyl alcohol, palmityloleoyl alcohol, stearyl alcohol, iso stearyl alcohol, oleyl alcohol, elaidyl alcohol, petroselnyl alcohol, linoloyl alcohol, linolenyl alcohol, elaeostearyl alcohol, arachyl alcohol, gadoleyl alcohol, behenyl alcohol, erucyl alcohol and brassidyl alcohol and technical mixtures thereof. Preferred wax esters are stearyl palmitate, stearyl stearate, stearyl isostearate, stearyl oleate, stearyl behenate, stearyl erucate, iso stearyl palmitate, iso stearyl stearate, iso stearyl isostearate, iso stearyl oleate, iso stearyl behenate, iso stearyl erucate, oleyl palmitate, oleyl stearate, oleyl isostearate, oleyl oleate, oleyl behenate, oleyl erucate, behenyl palmitate, behenyl stearate, behenyl isostearate, behenyl oleate, behenyl behenate, behenyl isostearate and mixtures thereof. Stearyl stearate is particularly preferred as the wax ester. It is important in this regard to bear in mind that stearyl stearate is normally produced from technical starting materials which in turn are mixtures so that the ester is also a mixture.

The esters mentioned may be obtained by known methods of organic synthesis, for example by heating stoichiometric quantities of fatty acid and fatty alcohol to 180-250°C, optionally in the presence of a suitable esterification catalyst, such as tin gradings, and in an inert gas atmosphere, and distilling off the water of reaction.

Suitable additional lubricants are polyol fatty acid esters, i.e. esters of C₁₂₋₂₄ fatty acids and polyols containing 4 to 6 hydroxyl groups. The alcohol component may be selected, above all, from aliphatic polyols containing 4 to 12 carbon atoms, for example erythritol, pentaerythritol, dipentaerythritol, ditrimethylol propane, diglycerol, triglycerol, tetraglycerol, trianitrol and sorbitol. These polyol esters may be full esters in which all the hydroxyl groups of the polyol are esterified with fatty acid. However, polyol partial esters containing one or more free hydroxyl groups in the molecule are also suitable. These polyol fatty acid esters may also be obtained by known methods of organic synthesis by esterification of the polyols with stoichiometric or sub-stoichiometric quantities of free fatty acids. Examples of such polyol fatty acid esters are the stearic acid and stearic acid/palmitic acid full esters of erythritol, pentaerythritol and diglycerol, the diolurates of dipentaerythritol, ditrimethylolpropane, triglycerol, trianitrol and sorbitol, the diesterates of erythritol, pentaerythritol, dipentaerythritol and tetraglycerol and the so-called sesquiterpentenol ethers.

Other suitable additional lubricants are complex esters which are also known per se from the prior art. In principle, the complex esters are produced from dicarboxylic acids, polyols and monocarboxylic acids.
The following dicarboxylic acids may be used for the production of the complex esters: oxalic, malonic, succinic, glutaric, adipic, pimelic, suberic, azelaic, sebacic, nonanedioic acid, undecanedioic acid, eicosanedioic acid, maleic, fumaric, citraconic, mesaconic, itaconic, cyclohexane dicarboxylic acid, cyclopentane dicarboxylic acid, camphor, hexahydrophthalic acid, phthalic, terephthalic, isophthalic, naphthalic and diphenyl o-o’-dicarboxylic acid. The following compounds are generally used as aliphatic polyols containing 2 to 6 hydroxyl groups: ethylene glycol, 1,2-propylene glycol, 1,3-propylene glycol, 1,4-butanediol, 2,3-butanediol, 1,5-pentanediol, 1,6-hexanediol, glycerol, trimethylolpropane, erythritol, pentaoxythitol, dipentaerythritol, xylitol, mannitol and sorbitol. Suitable monoalcoholic acids are linear or branched, synthetic or native acids, for example lauric, myristic, palmitic, margaric, stearic, arachic, behenic, lignoceric, cerotic acid, montanic acid, oleic, elaidic, erucic, linoleic, linolenic and isostearic acid and mixtures of these acids, particularly those obtainable from natural fats and oils. Preferred complex esters are produced from aliphatic dicarboxylic acids containing 4 to 8 carbon atoms, polyols containing 3 or 4 hydroxyl groups and aliphatic monocarboxylic acids containing 14 to 22 carbon atoms. Excellent results are obtained with complex esters of adipic acid, pentaoxythitol and monosubstituted acids containing 14 to 22 carbon atoms.

According to the invention, other suitable additional lubricants are dicarboxylic acid esters of fatty alcohols containing 12 to 24 carbon atoms. Suitable dicarboxylic acids have already been mentioned by way of example in connection with the complex esters. Suitable fatty acids are the fatty acids already discussed above. Phthalic acid esters, more especially distearyl phthalate, are particularly preferred.

Other additional lubricants, which may be used individually or in combination, are hydrocarbon waxes melting at temperatures in the range from 70 to 130°C, oxidized polyethylene waxes, α-olefins, ethylenediamine distearate, montanic acid esters of diols, for example ethanediol, 1,3-butanediol and glycerol, mixtures of such montanic acid esters with unesterified montanic acids and metal soaps, more particularly salts of organic monocarboxylic acids with metals of the second main and/or secondary group of the periodic system, such as calcium soaps and zinc soaps.

Accordingly, the present invention also relates to the use of lubricant combinations for thermoplastics containing

(a) one or more fatty acid polyethylene glycol esters (I) and

(b) one or more additional lubricants (not covered by formula (I)),

with the proviso that components (a) and (b) are used in a ratio by weight of 10:90 to 90:10 and preferably in a ratio by weight of 20:80 to 80:20.

The expression “lubricant combinations” applies both to lubricants and to internal lubricants.

In practice, the lubricant mixtures according to the invention are applied by addition to the thermoplastics to be processed in quantities of 0.05 to 5 and more particularly 0.1 to 2 parts by weight to 100 parts by weight of the thermoplastic. The lubricant mixtures are preferably added to the melt formed during production of the thermoplastic or are applied to the plastic granules or powder at elevated temperatures.

The thermoplastics may optionally contain additional additives. Examples of suitable additives are antistatic agents, fogging agents, antioxidants, UV stabilizers, coupling agents, calendering aids, parting agents, lubricants, plasticizers, perfumes, flame retardants, fillers and agents for increasing heat stability (heat stabilizers).

The thermoplastics may readily be further processed by standard methods, for example by extrusion, pressing, rolling, calendering, sintering, spinning, blow moulding, foaming, injection moulding or processing by the plastisol method.

**EXAMPLES**

1. Production of the Lubricants According to the Invention

Example 1

237 g diethylene glycol (Fluka), 1151 g technical stearic acid (Cognis) and 0.7 g tin(II) oxide (Goldschmidt) were heated under nitrogen. The esterification reaction began at ca. 170°C with the formation of water. After 3 hours, removal of the water of reaction was continued by application of vacuum, the vacuum being lowered to ca. 15 mbar over a period of 4 hours. The final temperature was 200°C.

The reaction was terminated at an acid value (AV) of <6. The reaction mixture was cooled to 90°C and filtered. Yield 1296 g, AV=1.6, SV (saponification value)=184.

Example 2

PEG-600 distearate was produced from 167 g PEG 600 (Fluka) and 147 g technical stearic acid (Cognis) in the same way as in Example 1. Yield 298 g, AV=5.9, SV=102.

2. Production of Dry Blends

Using a Henschel mixer, a dry blend was produced from PVC powder and various additives (quantity of material=3 kg, heating temperature=120°C, subsequent cooling). The compositions are set out in the following table (the numbers in the Table represent parts by weight).

<table>
<thead>
<tr>
<th>Example</th>
<th>C1</th>
<th>C2</th>
<th>C3</th>
<th>E3</th>
<th>E4</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVC Eviacl SH 6520 (Ineos)</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Pb sulfate, tribasic</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Lead stearate (28% Pb)</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>Calcium stearate</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>Hydrogenated castor oil</td>
<td>—</td>
<td>1.0</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Distearyl phthalate</td>
<td>—</td>
<td>1.0</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Lubricant of Example 1</td>
<td>—</td>
<td>—</td>
<td>1.0</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Lubricant of Example 2</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>1.0</td>
<td>—</td>
</tr>
</tbody>
</table>
In this Table, C1 to C3 are comparison Examples. In C1, no lubricant was added. In C2, hydrogenated castor oil was used; it is the most important internal lubricant for PVC bottles (cf. Plastics Additives Handbook, 5th Edition, Hanser Verlag, p. 537). In C3, distearyl phthalate—an internal lubricant for profile extrusion—was used. E4 and E5 represent formulations according to the invention.

### Production of Ribbons

The above-mentioned dry blends were extruded to ribbons in a Weber twin-screw extruder (extrusion parameters: screw speed=15 r.p.m., temperature=190° C.). The power consumed by the extruder, the machine load (in %), was evaluated as a measure of plasticization. Early plasticization leads to an increase in the machine load. The melt pressure (bar) before the die was used as a measure of lubricant performance. A low melt pressure signifies a good lubricating effect.

<table>
<thead>
<tr>
<th>Example</th>
<th>Machine load (%)</th>
<th>Melt pressure (bar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1</td>
<td>48.7</td>
<td>347</td>
</tr>
<tr>
<td>C2</td>
<td>56.6</td>
<td>354</td>
</tr>
<tr>
<td>C3</td>
<td>46.0</td>
<td>324</td>
</tr>
<tr>
<td>E4</td>
<td>51.1</td>
<td>344</td>
</tr>
<tr>
<td>E5</td>
<td>57.8</td>
<td>336</td>
</tr>
</tbody>
</table>

Examples E4 and E5 according to the invention led to earlier plasticization (increase in machine load) at a relatively low melt pressure than Comparison Example C1. Comparison Examples C2 and C3 lead either to better plasticization for an increase in melt pressure or impaire plasticization.

We claim:

1. A lubricated thermoplastic composition comprising:
   (a) thermoplastic polymer; and
   (b) a polyethylene glycol difatty acid ester lubricant of a formula:
   \[
   R^1-\text{CO}-\text{O}-\left(\text{CH}_2\text{CH}_2\text{O}\right)_n\text{OC}-R^2
   \]
   \[\text{(I)}\]
   in which \(R^1\) and \(R^2\) independently of one another represent alkyl groups containing 7 to 23 carbon atoms, which may be saturated or unsaturated, linear or branched, and \(n\) is a number of 2 to 50.
2. The lubricated thermoplastic composition of claim 1, wherein \(n\) is a number of 2 to 4.
3. The lubricated thermoplastic composition of claim 1, wherein \(R^1\) and \(R^2\) independently of one another are saturated alkyl groups containing 7 to 23 carbon atoms.
4. The thermoplastic composition of claim 1, wherein the lubricant is an internal lubricant.
5. The thermoplastic composition of claim 1, wherein the lubricant comprises a lubricant combination containing (a) at least one fatty acid polyethylene glycol ester (I) and (b) at least one additional lubricant (not covered by formula (I)), with the proviso that components (a) and (b) are present in a ratio by weight of 10:90 to 90:10.
6. The lubricated thermoplastic of claim 5, wherein (a) and (b) are present in a ratio by weight of 20:80 to 80:20.
7. The thermoplastic composition of claim 5, wherein the lubricant combination comprises an internal lubricant.
8. The lubricated thermoplastic of claim 1, wherein the thermoplastic comprises at least one member selected from the group consisting of polycarbonates, polyamides, polyesters, polystyrenes, polyvinyl chloride, and copolymers thereof.
9. A method of lubricating a thermoplastic which comprises: mixing with the thermoplastic a polyethylene glycol difatty acid ester lubricant of a formula:
   \[
   R^1-\text{CO}-\text{O}-\left(\text{CH}_2\text{CH}_2\text{O}\right)_n\text{OC}-R^2
   \]
   \[\text{(I)}\]
   in which \(R^1\) and \(R^2\) independently of one another represent alkyl groups containing 7 to 23 carbon atoms, which may be saturated or unsaturated, linear or branched, and \(n\) is a number of 2 to 50.
10. The method of claim 9, wherein, \(n\) is a member of from 2 to 4.
11. The method of claim 9, wherein, wherein \(R^1\) and \(R^2\) independently of one another are saturated alkyl groups containing 7 to 23 carbon atoms.
12. The method of claim 9, wherein, the lubricant is an internal lubricant.
13. The method of claim 9, wherein, the lubricant comprises: a lubricant combination containing (a) at least one fatty acid polyethylene glycol ester (I) and (b) at least one additional lubricant (not covered by formula (I)), with the proviso that components (a) and (b) are present in a ratio by weight of 10:90 to 90:10.
14. The method of claim 13, wherein, (a) and (b) are present in a ratio by weight of 20:80 to 80:20.
15. The method of claim 9, wherein, the thermoplastic comprises at least one member selected from the group consisting of polycarbonates, polyamides, polyesters, polystyrenes, polyvinyl chloride, and copolymers thereof.